

KAMZOLKIN, V.V.; BASHKIROV, A.N.; MARTYNES, M.

Study of the process of continuous oxidation of paraffin hydrocarbons
to alcohols. Trudy Inst.nefti 12:281-289 '58. (MIRA 12:3)
(Paraffins) (Oxidation) (Alcohols)

KAMZOLKIN, V.V.; BASHKIROV, A.N.; MARTYNES, M.

Study of the action of boric acid and boric anhydride on liquid phase
oxidation of paraffin hydrocarbons. Trudy Inst.nefti 12:290-296 '58.
(MIRA 12:3)

(Paraffins) (Boric acid) (Oxidation)

BASHKIROV, A.N.; LODZIK, S.A.; KAMZOLKIN, V.V.

Determining the composition of primary and secondary higher alcohols by
the dehydration method. Trudy Inst.nefti 12:297-298 '58.

(MIRA 12:3)

(Alcohols) (Dehydration (Chemistry))

KRYUKOV, Yu.B.; BUTYUGIN, V.K.; LIBEROV, L.G.; STEPANOVA, N.A.; BASHKIROV, A.N.

Synthesis of butyl alcohol containing radioactive carbon C¹⁴. Trudy
Inst.nefti 12:299-303 '58. (MIRA 12:3)
(Butyl alcohol) (Carbon--Isotopes)

AUTHORS: Bashkirov, A. N., Kamzolkin, V. V., 20-1-42/58
Sokova, K. M., Andreyeva, T. P.,

TITLE: On the Problem of the Oxidation Mechanism of Paraffinic Hydrocarbons in the Liquid Phase (K ~~vyprosu~~ o mekhanizme zhidkofaznogo okisleniya parafinovykh ~~uglevodorodov~~)

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr 1, pp. 149-152 (USSR)

ABSTRACT: This process is complicated and consists of a number of reactions taking place in parallel or successively. It is considered an established fact that this oxidation under mild conditions proceeds to water and carbonic acid through intermediate products of an incomplete oxidation (peroxides, alcohols, ketones, acids and others). A complicated mixture of oxygen-containing products develops. In an earlier paper (reference 1) the authors worked out the synthesis of higher alcohols of the aliphatic series by direct oxidation of paraffinic hydrocarbons in the presence of boric acid. The Shemism and the mechanism of individual stages has still to be determined. For this purpose the oxidation of a number of individual hydrocarbons was carried out and the composition of the alcohols produced was studied. A nitrogen-oxygen mixture (3,0 - 3,5% O₂) with addition of 5% boric acid (calculated on the initial hydrocarbon) under atmospheric pressure was

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used for the oxidation. The temperature was 165-170°C and the duration was 4 hours. The hydrocarbons are characterized in table 1, the oxides ("oxydates"?) in table 2. From the latter follows that alcohols represent the main product (about 70%) of the oxidation. For determining their composition and structure they were isolated from the oxides. Their characteristics are recorded in table 3. From this is to be seen that the alcohols have hydroxyl numbers corresponding to tri-, tetra-, pent- and hexadecanole and consequently the same number of carbon atoms in the molecule as each of the corresponding initial hydrocarbons. In order to prove this alcohols were reconverted to hydrocarbons, in order to compare the properties of the latter with the initial hydrocarbons. The comparison of the two types of hydrocarbons showed their identity in the case of every individual alcohol. From this result the conclusion may be drawn that alcohols containing the same number of carbon atoms in the molecule as the initial hydrocarbons predominantly develop in the oxidation of n-paraffinic hydrocarbons by molecular oxygen in the liquid phase and under the conditions described. The molecule of the initial hydrocarbons is on the whole not destroyed. The determination of secondary alcohols meets with great difficulties

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and does not lead to positive results. The methods known in publications (references 3,4) proved to be useless. In order to solve this problem the authors worked out a special method of the quantitative determination of primary and secondary alcohols. For this purpose alcohols were by means of chromic acid oxidized in the medium of glacial acetic acid. The accuracy of this method is about 5%. From the given results of analysis follows that predominantly secondary alcohols form in the reaction studied here (87,7 - 88,7 mol.%). The interaction of oxygen with the molecules of the paraffinic hydrocarbons of normal structure mainly takes place at the secondary carbon atoms. There are 4 tables, and 5 references, 3 of which are Slavic.

ASSOCIATION: Petroleum Institute AS USSR (Institut nefti Akademii nauk SSSR)
PRESENTED: June 26, 1957, by A.V. Topchiyev, Academician
SUBMITTED: June 26, 1957
AVAILABLE: Library of Congress
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Bashkirov, A. N.

AUTHORS: Bashkirov, A. N., Kamzolkin, V. V.,

20-2-24/66

TITLE: The Synthesis of Ethanol From Carbon Dioxide and Hydrogen (Sintez etanola iz dnuokisi ugleroda i vodoroda).

PERIODICAL: Doklady AN SSSR, 1958, Vol. 118, Nr 2, pp. 293-296 (USSR)

ABSTRACT: The catalytic reduction of carbon dioxide by means of hydrogen under normal pressure leads to the formation of carbon monoxide and hydrocarbons. Under pressure methanol (references 6-8) and a certain quantity of ethanol, propanol, butanol and other higher alcohols (references 9,10) on that occasion develop on oxide-catalysts. Therefore the authors want to realize a directed synthesis as mentioned in the title. The high-pressure apparatus used for this purpose was already often described (reference 11). The outgoing gases were led back into the synthesis. The catalysts were before the synthesis reduced by means of hydrogen. Various precipitated iron-, cobalt-, and nickel-catalysts as well as molten iron-catalysts with admixtures (K_2O , Al_2O_3 , SiO_2) and others were tried out. Molten iron-catalysts were the most stable. Table 1 shows the influence of temperature, pressure and the composition of the initial mixture upon the produced substances. The alcohol fraction (up to $94^{\circ}C$) yielded methanol, ethanol and n-propanol (table 2). Ethanol was represented in the

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largest quantity of all. About 1% of the condensate was formed by acids, 90% of them acetic acid. Further the product desorbed from the activated charcoal was investigated (tables 3,4). It had been adsorbed from the outgoing gases during the synthesis. During the investigations some data on the chemism of the synthesis under review were obtained. An essential peculiarity of the process is the fact that it takes place in stages. At first carbon monoxide forms in quantities which do not exceed those in the water gas. Carbon monoxide represents the main source of the oxygen-containing compounds and of hydrocarbons. The concentration of carbon monoxide decreases with increasing concentration of water vapor in the reaction mixture. The synthesis comes to a standstill when the concentration of carbon monoxide sank to about 2%. The recirculation is capable of largely suppressing the formation of carbon monoxide. Table 5 gives some data on the products obtained in this connection. An approximate material balance shows a yield per 1 m³ gas mixture (CO₂ : H₂ = 1 : 3) in gram of: alcohols 92, hydrocarbons 81 water 345, carbon monoxide 31 and other oxygen-containing compounds 10. A lower speed of passage leads to an increase in the amount of acids. This may be in favor of the conception that the

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main final product, ethanol, develops from acetic acid by reduction. This new synthesis of ethyl alcohol from carbon dioxide and hydrogen represents a step forward on the way of the development of the at present not yet numerous methods of converting carbon dioxide to valuable chemical products. There are 5 tables, 11 references, 4 of which are Slavic.

ASSOCIATION: Petroleum Institute, 'AS USSR (Institut nefi Akademii nauk SSSR)

PRESENTED: July 12, 1957, by A. V. Topchiyev, Academician

SUBMITTED: July 12, 1957

AVAILABLE: Library of Congress

Card 3/3

AUTHORS: Bashkirov, A. N., Kamzolkin, V. V. Sokova, K.M., 20-119-4-21/60
Andreyeva, T. P.

TITLE: The Composition of Alcohols Produced by Liquid Phase Oxidation of n-Paraffinic Hydrocarbons (O sostave spirtov, poluchayushchikhsya pri zhidkofaznom okislenii n-parafinovykh uglevodorodov)

PERIODICAL: Doklady Akademii Nauk SSSR, 1958, Vol. 119, Nr 4, pp. 705-707 (USSR)

ABSTRACT: The investigation of the chemical composition and the structure of higher aliphatic alcohols is very important for the explanation of their formation mechanism as well as for the selection of the right method for their rational exploitation. In the present paper the authors occupied themselves with the hydroxyl group in the alcohol molecule. They paid special attention to the method of oxidation of alcohols with sodium bichromate and with sulfuric acid. The weight ratios between alcohol and sodium bichromate were 1:3, the quantity of the diluted sulfuric acid and of alcohol 10:1. The oxidation was carried out at different temperatures. The existence of certain methyl ethers was found in single fractions. The

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computation could be carried out also according to the following formula:

$$X = \frac{A(M-1)-107.9(100-A)}{14A} \cdot 100$$

whereby X denotes the content of acid C_n (mol.%); A denotes the content of silver in the existing silver salt (percentage by weight); M denotes the molecular weight of the acid C_{n+1} ; The numerical empirical data prove that this method of oxidation of alcohols can be used very well for the detection of the position of the hydroxyl group. The experimental results show furthermore that the alcohols obtained form a binary mixture of n-hexadecyl alcohols. The quantity of various alcohol molecules in this group is equal. Comprisingly was said that the alcohols produced by the oxidation of n-paraffinic hydrocarbons are mainly of secondary nature and represent a mixture of various isomeric substances. The reactivity of the atoms of the molecules of higher paraffin hydrogens of normal structure does not display any considerable differences and is equal in comparison to oxygen. This is the condition for the production of isomeric substances

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of secondary alcohols during the oxidation process of hydrocarbons in liquid state.

There are 1 table and 5 references, 4 of which are Soviet.

ASSOCIATION: Institut nefiti Akademii nauk SSSR (Petroleum Institute of the AS USSR)

PRESENTED: December 14, 1957 by A. V. Topchiyev, Member, Academy of Sciences, USSR

SUBMITTED: December 14, 1957

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25-119-6-27/56

AUTHORS: Kryukov, Yu. B.; Bashkirov, A. N.; Butyugin, V. K.;
Liberov, L. G.; Stepanova, N. D.

TITLE: On the Uniformity of the Mechanism of Synthesis of Hydrocarbons and Oxygen Containing Compounds of CO and H₂
(O yedinstve mekhanizma sinteza uglevodorodov i kislorodsoderzhashchikh soedineniy iz CO i H₂)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 119, Nr 6, pp.1152-1155 (USSR)

ABSTRACT: For the synthesis of CO and H₂ different schemes were proposed. According to them both processes mentioned in the title proceed independent of each other in two different ways. (Refs 1-5). Contrary to this fact experimental data exist, which permit the assumption that a uniform mechanism exists in introducing the process of synthesis and in the structure of carbon chains of the aliphatic compounds from CO under the influence of hydrogen. In order to prove that, the authors have experimentally investigated the ways of conversion of alcohols under the real conditions of synthesis, if the primary products of syn-

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thesis represented a carbon-alcohol mixture. Butanol marked by C¹⁴ and methanol, which were added to the gas of synthesis in such quantities that the conditions existing on the surface of the catalyst were not disturbed, served as indicators of the behavior of the alcohols formed of CO and H₂. Molten iron catalysts under high pressure (100 - 150 atmospheres excess pressure) served for this purpose. Figure 1 shows typical results. From figure 2 is to be seen that methanol is much more easily subject to different conversions than butanol. From the totality of the obtained results follows that the processes of synthesis of hydrocarbons and oxygen containing compounds of CO and H₂ are connected with each other. On the molten iron catalysts the afore-mentioned compounds and the alcohols possess a common source of origin. This is an unstable intermediate complex on the surface of the catalyst, which forms during the primary interaction between CO and H₂. This complex contains C-, H- and O-atoms. It is named C₁ by the authors. It is able to condense with its equals, whereby the formation of the carbon-carbon bond, furthermore that of a new oxygen containing compound with 2 carbon-C₂-atoms

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is guaranteed. The further growth takes place thanks to the continuous connection of C₁ to the growing complexes C₂, C₃, C₄ and so on. Also the molecules CO and H₂ can be taken up and a further hydration of the growing complexes until the formation of a stable compound (aldehyde, alcohol, olefin, or paraffin) seems to be not impossible. There are 2 figures and 11 references, 3 of which are Soviet.

ASSOCIATION: Institut nefti Akademii nauk SSSR
(Petroleum Institute AS USSR)

PRESENTED: December 26, 1957, by A. V. Topchiyev, Member, Academy of Sciences, USSR

SUBMITTED: December 24, 1957

Card 3/3

BashKirov A.N.

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Abstracts from 1975. Scientific literature

Abstracts from 1975. Scientific literature. (Oxidation of hydrocarbons in the liquid phase; Collection of articles) Moscow, Ltd.-v. AS 828, 1975. 338 p. Extracts only inserted. 2,500 copies printed.

M.I. R. E. Zhurav, Corresponding Member, Academy of Sciences USSR, 24. of Publishing House: E. M. Zhurav, Tech. Ed.: E. F. Kur'ma.

Abstracts: This collection of articles is intended for chemists interested in hydrocarbon oxidation reactions, particularly for those specializing in petroleum fuels.

CONTENTS: This collection of 35 articles represents the results of investigations over a period of several years on problems of hydrocarbon oxidation. The authors present their own theoretical and experimental data and also draw from current literature. No personalization are mentioned. The collection is divided into two parts.

1. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 159
Oxidation of n-alkanes, n-pentadecane and n-hexadecane in the presence of boron acid is investigated. For the most part, second-order kinetics are found. The purpose of the study was to establish a relationship between the rate of oxidation and the structure of the hydrocarbon. The oxidation of paraffin hydrocarbons developed by the N.V. Zhurav Institute.

2. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 160
Liquid-phase oxidation of n-alkanes as a model reaction for normal paraffin hydrocarbons is studied. An optimum amount of cobaltous acetate (acetylacetonate, acetylacetonate, acetylacetonate, acetylacetonate) is obtained after passing 700-900 liters of air per hour through the reaction mixture for 10 hours at 150°.

3. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 161
The authors describe the oxidation of alkanes (hexane), the authors conclude that the oxidation process can be used to obtain alcohols.

4. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 162
The authors describe the oxidation of alkanes (hexane), the authors conclude that the oxidation process can be used to obtain alcohols.

5. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 163
The authors describe the oxidation of alkanes (hexane), the authors conclude that the oxidation process can be used to obtain alcohols.

6. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 164
The authors describe the oxidation of alkanes (hexane), the authors conclude that the oxidation process can be used to obtain alcohols.

7. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 165
The authors describe the oxidation of alkanes (hexane), the authors conclude that the oxidation process can be used to obtain alcohols.

8. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 166
The authors describe the oxidation of alkanes (hexane), the authors conclude that the oxidation process can be used to obtain alcohols.

9. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 167
The authors describe the oxidation of alkanes (hexane), the authors conclude that the oxidation process can be used to obtain alcohols.

10. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 168
The authors describe the oxidation of alkanes (hexane), the authors conclude that the oxidation process can be used to obtain alcohols.

11. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 169
The authors describe the oxidation of alkanes (hexane), the authors conclude that the oxidation process can be used to obtain alcohols.

12. Oxidation of n-alkanes, E.K. Zhurav, and T.P. Zhurav, (Inst. of Petrochemicals, USSR). 170
The authors describe the oxidation of alkanes (hexane), the authors conclude that the oxidation process can be used to obtain alcohols.

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AUTHORS:

Bashkirev, A. N., Kamzolkina, Ye. V., Kagan, Yu. B.

SOV/156-59-1-42/54

TITLE:

On Catalysts of the Reactions of the Decomposition of Carbon Monoxide (O katalizatorakh reaktsiy razlozheniya okisi ugleroda)

PERIODICAL:

Nauchnyye doklady vysshey shkoly. Khimiya i khimicheskaya tekhnologiya, 1959, Nr 1, pp 162 - 165 (USSR)

ABSTRACT:

For the systematic investigation of the influence of catalysts on the reactions: 1) $2 \text{Fe} + 2 \text{CO} \rightarrow \text{Fe}_2\text{C} + \text{CO}_2$, and 2) $2\text{CO} \rightarrow \text{C} + \text{CO}_2$, melted iron catalysts with activating additives (Al_2O_3 , SiO_2 , K_2O , Cr_2O_3 , B_2O_3 , MoO_3 , V_2O_5 , MgO , MnO , and combinations thereof), as employed in the synthesis $\text{Co} + \text{H}$, were investigated. The results are listed in a table. Carbide formation (reaction 1) and reaction 2 were accelerated by Al_2O_3 and V_2O_5 . K_2O accelerates only reaction 1. MoO_3 is ineffective, Cr_2O_3 , FeCr , and in particular SiO_2 and B_2O_3 exercise inhibitory effects. With several additives to the catalyst, the properties have, as a rule, a cumulative effect.

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Only FeCr, which, when added exclusively, inhibits the reaction, increases the reaction velocity in the presence of other additives. Thus an iron catalyst with kaolin (as an SiO_2 vehicle), K_2O and FeCr showed the highest reactivity.

In this case, even B_2O_3 inhibits only reaction 2. A further test series concerned industrial iron catalysts, which were also given additives. The table of the results shows that also in this case the same rules apply. There are 2 tables and 1 Soviet reference.

ASSOCIATION: Kafedra neftekhimicheskogo sinteza i iskusstvennogo zhidkogo topliva Moskovskogo instituta tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Chair of Petroleum-chemical Synthesis and Artificial Liquid Fuels of the Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: October 6, 1958

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5(3)

SCV/62-59-7-34/38

AUTHORS: Kagan, Yu. B., Bashkirov, A. N., Kliger, G. A., Yermakov, Yu. I.

TITLE: Transformation of n-Butyl Amine Under Synthesis Conditions From Carbon Oxide and Hydrogen (Prevrashcheniye n.butilamina v usloviyakh sinteza iz okisi ugleroda i vodoroda)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 7, pp 1345 - 1346 (USSR)

ABSTRACT: It had been found in previous investigations that when synthesizing n-butyl amine from CO, H₂ and NH₃ in the presence of iron catalysts, di- and trialkyls are formed in addition to monoalkyl amines. Moreover, the formation of the di- and trialkyls was found to be dependent in the course of reaction by the facilitated reacting possibility of primary amines with oxygen-containing products from the hydrogenation of the carbon oxide (alcohols, aldehydes, etc). The conclusion was drawn therefrom that the secondary and tertiary amines may be obtained from CO, H₂, and the primary amine, here n-butyl amine. This conclusion is submitted to examination in the

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present paper. The synthesis conditions were the same as in references 1 and 2. A molten iron catalyst was also used in the investigation. The amines obtained were potentiometrically titrated. The following was investigated in the course of synthesis: the influence exerted by the amine addition rate upon the catalyst, by temperature, pressure, and the ratio CO/H in the initial mixture on the yield and the products of the synthesis. The data obtained are specified in the table. It may be observed from the latter that secondary and tertiary amines may be actually obtained in the manner described, and that, by changing the conditions, the reaction may be directed to the production of either secondary or tertiary amines. Increase in the concentration of n-butyl amine and temperature leads to the predominant formation of secondary amine, dilution of hydrogen, low temperature, and slow addition of n-butyl amine on the catalyst for the formation of tertiary amine. Rising pressure increases the formation of the two amines. At 80-150° the largest percentage yield of secondary and tertiary amines is obtained (45%). The additionally obtained primary amine (50%) is caused by disproportionation. There are 1

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table and 10 references, 7 of which are Soviet.

ASSOCIATION: Institut nefiti Akademii nauk SSSR (Institute of Petroleum
of the Academy of Sciences, USSR)

SUBMITTED: January 19, 1959

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KAGAN, Yu.B.; BASHKIROV, A.N.; MOROZOV, N.G.; KRYUKOV, Yu.B.; ROZOVSKIY, A.Ya.

Hydrogenating capacity of fused iron catalysts in the synthesis
from CO and H₂. Trudy Inst.nefti 13:167-179 '59. (MIRA 13:12)
(Catalysts) (Hydrogenation)

BASHKIROV, A.N.; LOKTEV, S.M.; KAGAN, Yu.B.; SABIROVA, G.V.

Hydrogenation of compounds containing a carbonyl group (over fused
iron catalysts). Trudy Inst.nefti 13:180-195 '59. (MIRA 13:12)
(Carbonyl compounds) (Hydrogenation)
(Catalysts)

5 (3)

AUTHORS:

Kamzolkin, V. V., Bashkirov, A. N.,
Corresponding Member AS USSR,
Potarin, M. M.

SOV/20-126-6-38/67

TITLE:

On the Synthesis of Higher Ketones by Means of the Oxidation of
Paraffin Hydrocarbons (O sinteze vysshikh ketonov metodom oki-
sleniya parafinovykh uglevodorodov)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 126, Nr 6, pp 1282 - 1285
(USSR)

ABSTRACT:

The formation of the carbonyl compounds takes place in the ox-
idation of the paraffin hydrocarbons at 120-160° much more ra-
pidly in the initial stage than the formation of the alcohols
and acids. On the basis of the concepts on the order of the for-
mation of oxygen containing compounds (see scheme, Refs 1,2) it
may be maintained that in this case ketones are formed mainly
directly from hydroperoxide. Because of this observation ex-
periments were carried out to determine whether a directed syn-
thesis of higher ketones by means of the oxidation of paraffin
hydrocarbons is possible in the liquid phase. For this purpose
the authors studied the action of the reaction conditions as
well as of some additions on the rate of oxidation and on the

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composition of some forming products. The fraction of synthetic hydrogenated paraffin hydrocarbons which boils out between 105 and 130° (1 torr) and which consists of carbons with 16 to 18 carbon atoms, was oxidized. The apparatus used and the method applied are described in reference 3. The temperature effects are shown by table 1. Their increase to 165° considerably intensifies the conversion of the initial hydrocarbons. A further increase to 185° remains practically without effect. The maximum yield of ketones was obtained at 120-140°. Also in the oxidation by a nitrogen oxygen mixture (3.5% O₂) the above regularities existed. By increasing this content to 21% O₂ the ketone portion in the reaction products decreased (Table 2). At the same time, however, the degree of conversion of the initial hydrocarbons increased. It is possible that other oxidation conditions may be found under which high ketone yields are obtained. Such e.g. the reduction of the specific consumption of the oxidizing gas (oxygen) from 1000 l/kg .^h to 200 l/kg .^h leads to ketone yields of about 55% computed with respect to the reacted paraffin (Table 2). Table 3 shows the effect exercised by

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the duration of oxidation on the composition of the oxide (3.5% O_2+N_2 at 140°). The oxidation intensity increases and the ketone yield decreases with the longer duration. The optimum duration is 3-4 hours in the oxidation with air at 140° . It may be seen from figure 1 that at 120° the oxidation is inhibited after a certain maximum degree of conversion (which depends on the reaction conditions) is attained. Later, the ketone and acid portion increases somewhat at the expense of the alcohol portions (Fig 1 and experiments Nr 1,2,4,5 in table 2). In this case an alcohol oxidation may take place. The oxidation process of the hydrocarbons concerned takes place according to the chain mechanism of the free radicals where a bimolecular decomposition of hydroperoxide leads to a branching of the chain, see scheme (Ref 4). The self-acceleration of the reaction at relatively low temperatures is due to the peroxide decomposition. The oxidation rate depends on the formation rate and the concentration of the free radicals in the reaction zone. The decomposition may take place also due to an interaction with the radical of reaction III according to reference 1. The mentioned inhibition is

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probably due to a rapid reduction or stoppage of the formation of free radicals which are responsible of the reaction course. At higher temperatures no inhibition occurs and the oxidation takes place to a considerable degree of conversion (Fig 2). Alcohols, esters, acids and other oxygen containing compounds accumulate, however, in high quantities. Additions of KMnO_4 , FeSO_4 etc. could not bring about an increase of the ketone yield. The results obtained indicate that the formation of free radicals takes place mainly according to reaction (III) and not according to (I) and (II). Thus, it was proved that the higher aliphatic ketones may be produced by direct oxidation of paraffin hydrocarbons with yields of approximately 65 mol% of the transformed hydrocarbon and at a degree of conversion of 10-15 mol%. There are 2 figures, 3 tables, and 5 references, 3 of which are Soviet.

*ASSOCIATION: Institut neftekhimicheskogo sinteza Akademii nauk SSSR (Institute of Petrochemical Synthesis of the Academy of Sciences, USSR)

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5(2)

AUTHORS: Bashkirov, A. N., Corresponding Member, SOV/20-127-1-24/65
AS USSR, Potarin, M. M., Kamzolkin, V. V.

TITLE: The Synthesis of Higher Ketones by Liquid Phase Oxidation of Secondary Alcohols (Sintez vysshikh ketonov metodom zhidko-faznogo okisleniya vtorichnykh spirtov)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 1, pp 93-96 (USSR)

ABSTRACT: The oxidation of the paraffin hydrocarbons in the liquid phase is considered to be a process of various stages. The succession of these stages is shown by a scheme (Refs 1-3). A considerable number of carbonyl compounds are formed, as a rule, in the production of synthetic sebacic acids by the oxidation of solid paraffins. The oxidation products of the higher paraffin hydrocarbons contain besides secondary alcohols (in the presence of boric acid) always a certain quantity of ketones (Ref 5). The carbonyl compounds (see Scheme) may be produced : a) by the decomposition of hydroperoxide (Ref 6); b) by the oxidation of the alcohols in the reaction zone. The authors attempted to clarify the possibility of oxidizing the alcohols to ketones under conditions similar to those of the oxidation of

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hydrocarbons in the liquid phase, furthermore, the possibility of an orientated oxidation of secondary alcohols to ketones. For this purpose higher aliphatic alcohols (fraction boiling out within the range of from 125-170°, produced according to the method of reference 5) were used with a content of secondary alcohols of approximately 90 mole% (Ref 7). The apparatus and the method were already earlier described (Ref 5). The quantity of acids in the reaction products increases with rising temperature in the oxidation by means of an oxygen-nitrogen mixture (6.0-6.5 wt% O₂) during 4 hours at 120-180°, in contrast to that of ketones which is reduced from 63.6 to 55.3 mole% (Table 1). Carbonyl compounds apparently cannot be accumulated in greater quantities at higher temperatures since they are rapidly oxidized to acids. These acids occur either free or as esters. The transformation degree of the initial alcohols is increased by the increase of O₂-concentration in the reaction zone, the relative yield of ketones, however, is reduced (Table 2). The reaction rate depends as a rule to a considerable extent on the O₂-concentration in the oxidizing

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The Synthesis of Higher Ketones by Liquid Phase
Oxidation of Secondary Alcohols

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gas. Its increase leads to greater yields of acids. The prolongation of the oxidation (Table 3, Fig 1) increases the transformation degree of the alcohols and the acid yield at the expense of the ketone yield. On the strength of the experimental results an oxidation method for alcohols could be chosen which guaranteed a ketone yield of 60 mole% in the case of a transformation degree of 40-45 mole% of alcohols; i.e.: temperature 165°, O₂-content in the gas mixture

60-65 %, the specific consumption of the latter 1,000 l/kg^h, oxidation duration 3 hours. A higher yield of ketones may be obtained in the case of a lower transformation degree of the alcohols. Additions of Co-, Ni-, Mn-, Fe-, Cr-, Cu-, and Sn-salts are ineffective. Iron pentacarbonyl has a considerably inhibiting effect on the reaction. This proves its radical character. The data obtained are well in line with reference 8 with respect to the effect of boric acid and boric anhydride on the process mentioned in the title. There are 1 figure, 3 tables, and 8 Soviet references.

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The Synthesis of Higher Ketones by Liquid Phase
Oxidation of Secondary Alcohols

SOV/20-127-1-24/65

ASSOCIATION: Institut neftekhimicheskogo sinteza Akademii nauk SSSR
(Institute of Petrochemical Synthesis of the Academy
of Sciences, USSR)

SUBMITTED: March 16, 1959

Card 4/4

66172

~~5(3)~~ 5. 3400

AUTHORS: Kamzolkin, V. V., Bashkirov, A. N., Corresponding Member, AS
USSR, Sokova, K. M., Andreyeva, T. P. SOV/20-128-5-26/67

TITLE: On the Composition of Ketones Formed in Oxidation in the
Liquid Phase From n-Paraffin Hydrocarbons

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 5,
pp 956 - 959 (USSR)

ABSTRACT: Secondary alcohols with a normal structure are the main
products in the oxidation of n-paraffin hydrocarbons by mole-
cular oxygen in the liquid phase under mild conditions in the
presence of boric acid (Refs 1-3). The molecules of these
alcohols have the same number of carbon atoms as the initial
hydrocarbon. These alcohols form a mixture of all isomers
possible with regard to the position of the hydroxyl group.
Compounds with a carbonyl group, acids, and polyfunctional
compounds are formed as side products. The authors paid special
attention to the carbonyl compounds and used n-hexadecane
as initial product. Its oxidation took place in a device de-
scribed in reference 2. The oxidized substances enumerated in
table 1 were formed by the effect of a nitrogen-oxygen mixture

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On the Composition of Ketones Formed in Oxidation
in the Liquid Phase From n-Paraffin Hydrocarbons

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(with 3.5% O_2) at 165-170° and 5% boric acid within 4 hrs.

Among them were ~ 19 mol% compounds with a carbonyl group. The carbonyl compounds were separated from the oxidized substance for the purpose of determining their composition. About 40% of their total amount remained with the products which had reacted with boric acid. For this reason the authors assume that the afore-mentioned compounds containing carbonyl consist of ketones and polyfunctional compounds with a carbonyl group (mainly ketoalcohols). The distillate was chromatographically separated into paraffin hydrocarbons and compounds containing oxygen in order to determine the composition of the ketones. Table 2 shows the melting temperatures of semicarbazones. Comparison with them did not yield a final conclusion regarding the composition of the ketones investigated. Thus, they were oxidized with potassium bichromate in diluted H_2SO_4 (Ref 3).

Table 3 shows the results of the rectification of the methyl esters of the acids formed in the oxidized substance. Table 4 shows the weight- and per cent ratios of these acids. On account of the above results, the authors ascertain that mainly

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On the Composition of Ketones Formed in Oxidation
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ketones are represented among carbonyl compounds in the reaction mentioned. These ketones have the same chain length as the initial hydrocarbon. They form a mixture of all isomers theoretically possible with regard to the position of the carbonyl group. Polyfunctional compounds containing a carbonyl group are formed in addition to the ketones. There are 4 tables, and 4 references, 3 of which are Soviet.

ASSOCIATION: Institut neftekhimicheskogo sinteza Akademii nauk SSSR (Institute of Petroleum-chemical Synthesis of the Academy of Sciences, USSR)

SUBMITTED: June 26, 1959

Card 3/3

66417

~~5(2,3)~~ 5. 3400

AUTHORS: ~~Bashkirov, A. N.~~ Corresponding Member SOV/20-128-6-21/63
AS USSR, Shiman Pal

TITLE: Liquid-phase Oxidation of Olefines in the Presence of Boric Acid

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 6, pp 1175 - 1178 (USSR)

ABSTRACT: The molecule of the initial hydrocarbon is not destroyed in the initial stage of oxidation of the hydrocarbons of normal structure (stage of alcohol formation) (Refs 1,2). Under the conditions chosen by the authors, secondary alcohols are primarily formed in the presence of boric acid. They form a mixture of all possible isomers with the same number of carbon atoms in the molecule as there had been in the initial hydrocarbon. As the isomers mentioned are formed in equal molar quantities, it appears that the reactivity of the secondary carbon atoms in the molecule of the higher paraffin hydrocarbons is practically the same with respect to the oxygen. Primary alcohols with the same C-atom number as in the initial substance are missing in the oxidation products of normal paraffin hydrocarbons. This is apparently due to the higher stability of the C-H-bond in the

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Liquid-phase Oxidation of Olefines in the Presence of
Boric Acid

66417

SOV/20-128-6-21/63

methyl group as compared with the methylene groups. The authors oxidized synthetic n-dodecene-1. The pressure of the normal nitrogen-oxygen mixture was normal, the O_2 -content was about 4%, boric acid 5-7%, temperature 165-175°, duration 2-3 hours. The apparatus was described in reference 1. The oxidates obtained are characterized in table 1. Table 2 presents the hydroxyl-containing products of this reaction. Alcohols (about 75 molar %) were formed as a main product at an oxidation intensity of about 27%. Table 2 suggests that the 1st fraction (about 38% of the hydroxyl-containing compounds) represents n-nonyl alcohol, which was confirmed later on. The 2nd fraction had - besides a high hydroxyl number - also a high iodine number. This fraction primarily consists of unsaturated alcohols $C_{12}H_{23}OH$. By selective hydrogenation and acid formation (Ref 2), several acids were isolated and identified (Table 3). Hence it was found that the alcohols of this fraction represent a mixture of unsaturated secondary alcohols. About 60 molar % fall to the share of dodecenol-3, the remaining 40% are represented by other possible isomers of the alcohol group $C_{12}H_{23}OH$. The 3rd fraction was a

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SOV/20-128-6-21/63

crystalline substance: n-dodecanol-1,2. Synthetic n-dodecene-2 was oxidized in addition. The results show that the double bond in the carbon molecule considerably influences the direction of oxidative transformations. The formation of glycol suggests an analogy in the oxidation process with Prilezhayev's reaction. There are 4 tables and 8 references, 7 of which are Soviet.

ASSOCIATION: Institut neftekhimicheskogo sinteza Akademii nauk SSSR (Institute for the Chemical Synthesis of Petroleum of the Academy of Sciences, USSR). Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: June 26, 1959

Card 3/3

BASHKIROV, A.N.; KAMZOLKIN, V.V.; SOKOVA, K.M.; ANDREYEVA, T.P.

Determination of primary and secondary higher alcohols of
the aliphatic series in their mixtures. Metod.anal.org.
soed.nefti,ikh smes. i proizv. no.1:170-177 '60. (MIRA 14:8)
(Alcohols) (Hydrocarbons)

38689

S/510/60/014/000/003/006
D244/D307

5.3300

AUTHORS: Kamzolkin, V.V., Bashkirov, A.N., Sokova, K.M., and
Andreyeva, T.P.

TITLE: Composition of oxygen-containing compounds forming during
the liquid phase aerial oxidation of n-pentadecane

SOURCE: Akademiya nauk SSSR. Institut nefti. Trudy, v. 14, 1960,
Khimiya nefti, 65 - 75

TEXT: Results are presented of the study of the composition of the
products of oxidation of n-pentadecane in the presence of boric
acid. More oxygen was used in this work than previously (Bashkirov
A.N., Khimicheskaya nauka i promyshlennost', 1, no. 3, 272 (1956)).
The aim of the present investigation was to obtain additional data
on the oxidative conversions of hydrocarbons and on some intermedia-
te oxygen-containing compounds. It was found that the increase of O
in the oxidizing gas from 3.5 % to 21 % doubles the quantity of O -
containing compounds. At the same time the proportion of OH - con-
taining compounds decreases from 70 % to 50 % and COOH - containing
compounds increase from 12 % to 31 %. The amount of carbonyl com-
Card 1/2

S/510/60/014/000/004/006
D244/D307

AUTHORS: Bashkirov, A.N., Loktev, S.M., Sabirova, G.V., and
Novak, F.I.

TITLE: Composition of liquid products of the synthesis from CO
and H₂ on talc catalysts

SOURCE: Akademiya nauk SSSR. Institut nefti, Trudy, v. 14, 1960,
Khimiya nefti, 76 - 84

TEXT: Results are presented of the chemical composition of CO - H₂
synthesis on talc catalysts and of the influence of the chemical
composition of the catalysts and the synthesis conditions on the com-
position of the reaction products. It was found that the products
were a complex mixture of alcohols, hydrocarbons, aldehydes, ketones
and small quantities of acids and esters. The water of the reaction
contained 1.2 % of organic acids and 12.5 % of neutral O-containing
compounds (alcohols and ketones). There were about 30 % of carbonyl
compounds in the products. Addition to the catalyst of .25 % of cal-
cium aluminate increased the ketone content to 36.6 % - 39.7 %. With
Card 1/2

Composition of liquid products of ...

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D244/D307

50 % of barium aluminate the content increased to 40 - 55 %. Selective hydrogenation of the liquid products could give liquids containing 75 - 80 % alcohols. The O-containing compounds before and after hydrogenation, contained unsaturated bonds. Increase of the space velocity from 100 h⁻¹ to 500 h⁻¹ gave 1.5 - to 4-fold increase in the alcohol content of the products and a decrease in the content of unsaturated compounds. Further increases to 1000 h⁻¹ gave only small changes in the yields and composition of the products. Regeneration of the catalyst by air at 380 - 450° enabled the authors to conduct the reaction at lower temperatures. Increase of the reaction temperature from 350 - 375°C to 400 - 430°C gave some increase in the content of alcohols, ketones, complex esters and carboxylic acids in the products and a decrease of the content of unsaturated compounds. There are 8 tables.

Card 2/2

S/195/60/001/002/006/010
B004/B067

AUTHORS: Kryukov, Yu. B., ~~Bashkirov, A. N.~~, Liberov, L. G.,
Butyugin, V. K., Stepanova, N. D., Kagan, Yu. B.

TITLE: Conversions of Iron Carbide Under the Conditions of the
Synthesis of Hydrocarbons From Carbon Monoxide and Hydrogen

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 2, pp. 274 - 281

TEXT: The present paper was presented at the All-Union Conference on Organic Catalysis in November 1959. The authors attempted to explain the part played by carbides as intermediate compounds in the synthesis of hydrocarbons. They used a standard iron catalyst with chromium admixture, which was reduced at 1000°C and activated at 300°C and 20 atm with the initial gas mixture CO + H₂ (1 : 1), which contained C¹⁴O. The catalyst, enriched with radioactive iron carbide, was then treated with pure CO + H₂. The radioactivity of the products formed was then measured. The authors found that mainly the following reactions took place in iron

✓

Card 1/2

Conversions of Iron Carbide Under the
Conditions of the Synthesis of Hydrocarbons
From Carbon Monoxide and Hydrogen

S/195/60/001/002/006/010
B004/B067

carbide (90%); hydrogenation to methane, exchange of C isotopes between CO and carbide. The rate of these reactions is low as compared to that of the synthesis reaction. Of 3000 CO molecules, only one exchanges its carbon; of 3000 CH₄ molecules, only five are formed by carbide hydrogenation. Hence, only 0.03% of the hydrocarbons with C > 1 was formed under the action of carbide. These data rebut the hypothesis according to which carbide products are intermediates in hydrocarbon synthesis from CO and H₂. There are 2 figures, 2 tables, and 22 references: 13 Soviet, 5 US, 1 British, and 3 German. ✓

ASSOCIATION: Institut neftekhimicheskogo sinteza AN SSSR (Institute of Petrochemical Synthesis of the AS USSR)

SUBMITTED: January 23, 1960

Card 2/2

S/195/60/001/003/008/013
B013/B058

AUTHORS: Kagan, Yu. B. Bashkirov, A. N., Kamzolkina, Ye. V.,
Loktev, S. M.

TITLE: On the Activation Process of Molten Iron Catalysts for
for CO and H₂ Synthesis Under the Effect of the Reaction
Mixture

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 3, pp. 393 - 400

TEXT: The activation of molten iron catalysts for the hydrocarbon
synthesis from CO and H₂ under the effect of the reaction mixture was
studied in this paper. The following catalysts were used:

- 1) $100\text{Fe}_3\text{O}_4 + 6\text{Al}_2\text{O}_3 + 4.2\text{SiO}_2 + 1.2\text{K}_2\text{O} + 0.3\text{Cr}$;
- 2) $100\text{Fe}_3\text{O}_4 + 6\text{Al}_2\text{O}_3 + 4.2\text{SiO}_2 + 1.2\text{K}_2\text{O} + 0.5\text{V}$;
- 3) $100\text{Fe}_3\text{O}_4 + 6\text{Al}_2\text{O}_3 + 4.2\text{SiO}_2 + 1.2\text{K}_2\text{O} + 1.0\text{B}_2\text{O}_3$. They were reduced

Card 1/4

On the Activation Process of Molten Iron
Catalysts for CO and H₂ Synthesis Under the
Effect of the Reaction Mixture

S/195/60/001/003/008/013
B013/B058

within 1.5 hrs in hydrogen current at 1000°C. The study was made in a highpressure apparatus (Ref. 4) in the laboratory. For each of the catalysts studied, the lowest temperatures and pressures were initially chosen, at which, over the freshly and reduced catalysts (in comparable time intervals), a high degree of transformation of the carbon monoxide (84 to 86%) entering at a volume rate of the initial gas (CO and H₂ 1 : 1) of $\sim 1500 \text{ h}^{-1}$ was obtained. The catalysts were gradually activated under these conditions. The duration of the tests varied. The tests of catalysts of equal composition were conducted under the same conditions and in the same reaction vessel. The indices of the synthesis were well reproducible. The results determined could therefore also be compared with each other. The samples were hydrogenated after termination of the synthesis test. Subsequently, the hydrogenated samples were treated with CO at atmospheric pressure, a volume rate of 800 h^{-1} and temperatures by 10° higher than at the end of the synthesis test, with carbide being formed. The studies

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On the Activation Process of Molten Iron
Catalysts for CO and H₂ Synthesis Under the
Effect of the Reaction Mixture

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B013/B058

produced the following results: the previously (Refs. 1, 2) made statement that the iron catalysts molten at high temperatures (1000°C) immediately after reduction, are inactive in the synthesis of CO and H₂ and obtain activity only during the course of this synthesis, was confirmed. Activation also continues after reaching activity, which warrants a practically complete transformation of the initial carbon monoxide. This process is not terminated until 3 to 4 days after conduction of the synthesis. Simultaneously with the activation of the catalysts under the effect of the reaction mixture, their reactivity with respect to carbide formation is also increased. Those catalysts which have reached equal activity in consequence of the CO + H₂ synthesis, have also a similar reactivity with regard to carbide formation. The activation of the catalysts during the synthesis is accompanied by an increase of their activity during CO decomposition under formation of elementary carbon. The conditions under which the activation of catalysts occur (pressure, temperature, CO₂ content of the gas) have a noticeable effect on their properties. Of the methods investigated of

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On the Activation Process of Molten Iron
Catalysts for CO and H₂ Synthesis Under the
Effect of the Reaction Mixture

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the activation of the catalyst for the synthesis, its treatment at the
synthesis temperature is suited best. In this case the catalysts get speci-
ally active, but simultaneously show a lower activity with regard to CO
decomposition. There are 3 figures, 4 tables, and 6 Soviet references.

ASSOCIATION: Institut neftekhimicheskogo sinteza AN SSSR
(Institute of Petrochemical Synthesis AS USSR)

SUBMITTED: January 19, 1960

Card 4/4

AUTHORS: Bashkirov, A. N., Corresponding S/020/60/131/04/030/073
Member, AS USSR, Kistanova, A. I. B011/B017

TITLE: Oxidation of Naphthene¹ Hydrocarbons in the Liquid Phase in the Presence of Boric Acid

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 4, pp 827-829 (USSR)

TEXT: Under the conditions mentioned in the title, the oxidation of naphthenes takes place widely under the formation of alcohols. For the purpose of studying this oxidation, the authors synthesized (according to Grignard) a series of naphthene hydrocarbons with side chains of varying lengths in the molecule: n-amylcyclohexane, n-heptylcyclohexane, and n-nonylcyclohexane. Their constants are shown in table 1. These compounds were oxidized at normal pressure by means of a nitrogen-oxygen mixture (O₂-content 3.5%). The specific consumption of the oxidizing gas was 1000 l/kg.h, the temperature 165°, the duration of the experiment 4 h, the added amount of boric acid 5%. The apparatus used was described in reference 1. The oxidized substance was saponified with hot water. Table 2 gives the characteristics of the oxidized substances. They show that the reaction products are mainly alcohols. After having saponified the boric acid esters, the not reacted hydrocarbons were separated chromatographically on silica gel of type ASK from the oxygen-containing compounds. Petroleum ether (boiling out at 60°) and methanol were used as displacing liquids. The esters were saponified by means

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Oxidation of Naphthene Hydrocarbons in the Liquid
Phase in the Presence of Boric Acid

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B011/B017

of caustic potash. The alcohols obtained were separated from ketones by the formation of boric acid esters. Bifunctional compounds which are formed in small quantities during oxidation were separated chromatographically (this method devised by the authors will be published shortly). Here benzene and methanol were used as displacing liquids. Pure alcohols were distilled in the vacuum (Table 3). Their primary and secondary alcohol content was determined (Table 4). Furthermore, the authors wanted to find out whether the oxidation described takes place under the destruction of the molecule. For this purpose, they dehydrated the alcohols which they obtained from the oxidized product of n-nonylcyclohexane over anhydrous aluminum oxide at 270° in the vacuum. The unsaturated hydrocarbons formed had an iodine number of 120 (for $C_{15}H_{30}$ it should be 122). They were hydrogenated in n-heptane medium over a Raney nickel catalyst at a hydrogen pressure of 30 atm and at 180° . n-Heptane was distilled off in the vacuum. Table 5 shows the comparative characteristics of the hydrocarbon obtained from alcohols and of the n-nonylcyclohexane used. These two substances are identical. Thus, the authors proved that alcohols are formed by oxidation of naphthenes with a side chain of normal structure in the presence of boric acid. In this case, no destruction of the molecule of the oxidized substance takes place. The alcohols formed are mainly secondary, and have the same number of carbon atoms in the molecule as the hydrocarbon used. ✓

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Oxidation of Naphthene Hydrocarbons in the Liquid
Phase in the Presence of Boric Acid

S/020/60/131/04/030/073
B011/B017

There are 5 tables and 4 references, 3 of which are Soviet.

ASSOCIATION: Institut neftekhimicheskogo sinteza Akademii nauk SSSR
(Institute of Petroleum-chemical Synthesis of the Academy of
Sciences, USSR). Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical
Technology imeni M. V. Lomonosov)

SUBMITTED: October 20, 1959

Card 3/3

5.3400

69993

AUTHORS: Bashkirov, A. N., Corresponding Member of S/020/60/131/05/022/069
the AS USSR, Kamzolkin, V. V., Potarin, B011/B117
M. M., Kolovertnov, G. D.

TITLE: Preparation of Higher Aliphatic Ketones by the Method of
Dehydrogenation of Secondary Alcohols

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 5, pp 1067-1068 (USSR)

TEXT: The topic mentioned in the title has been studied using an industrial-type skeleton nickel catalyst. It was proved by the authors that it is possible to obtain a high yield (85% by weight), if the above-mentioned liquid-phase preparation method is used. The amount of the catalyst was 10% of the alcohol. Commercially produced C₁₆ - C₁₉ alcohols containing 6% of hydrocarbons were dehydrogenated. The reaction temperature was 185°, the residual pressure 33 torr. From the kinetic curves of the reaction it follows that the reaction proceeds rapidly in the liquid phase, and is practically completed within two hours. The conversion degree of the alcohols reaches 95 mole % (Fig 1). At first, a vigorous separation of hydrogen takes place, the iodine number of the product decreases, probably as a result of the hydrogenation of the unsaturated compounds in the alcohols used. Then, the iodine number is somewhat increased which is due to a side reaction involving the dehydration of the alcohols. It could be established

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Preparation of Higher Aliphatic Ketones by the
Method of Dehydrogenation of Secondary Alcohols

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B011/B117

by chromatography on silica gel that the carbohydrate content was thereby increased from 6 to 10% by weight. The acid and ester content in the reaction products remains the same as the one in the alcohols used. The curves in figure 2 show that the dehydrogenation of the alcohols is accelerated by higher temperatures. Low pressure (33 torr) favors the reaction. The small quantity of unreacted alcohols was removed from the dehydrogenation product by esterification with boric acid. Substances not reacting with boric acid were distilled from the boric esters in vacuo (7 torr). The boiling-point range of the distillate was 115 to 120°. After removal of the hydrocarbons by means of chromatography on silica gel, a fraction of higher aliphatic ketones with d_4^{20} 0.8362, n_D^{20} 1.4446 and a carbonyl number of 202.0 was obtained. There are 2 figures and 5 references, 4 of which are Soviet.

ASSOCIATION: Institut neftekhimicheskogo sinteza Akademii nauk SSSR (Institute
of Petroleum-chemical Synthesis of the Academy of Sciences of the
USSR)

SUBMITTED: November 30, 1959

Card 2/2

KAGAN, Yu.B.; BASHKIROV, A.N.; KLIGER, G.A.

Amination of n-butanol over iron catalysts under hydrogen pressure.
Izv.AN SSSR Otd.khim,nauk no.3:468-473 Nr '61. (MIRA 14:14)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Butyl alcohol) (Amination)

KAMZOLKIN, V.V.; BASHKIROV, A.N.; KHOTIMSKAYA, M.I.; GROZHAN, M.M.;
YEZHENKINA, G.M.

Synthesis of aliphatic C₆ - C₁₀ alcohols by the liquid phase
oxidation of paraffins under pressure. Neftekhimiia 1 no.2:
244-254 Mr-Apr '61. (MIRA 15:2)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Alcohols) (Oxidation) (Paraffins)

KAMZOLKIN, V.V.; BASHKIROV, A.N.; LODZIK, S.A.

Composition of alcohols obtained by the direct oxidation of
paraffins under industrial conditions. Neftekhimiia 1 no.2:
260-266 Mr-Ap '61. (MIRA 15:2)

(Alcohols)
(Paraffins)

KLIGER, G.A.; BASHKIROV, A.N.; BEZINGER, N.N.; KAGAN, Yu.B.

Method for analyzing products obtained by the interaction
of aliphatic alcohols with ammonia in the presence of
hydrogen. Neftekhimia 1 no.3:397-402 My-Je '61.

(MIRA 16:11)

1. Institut neftekhimicheskogo sinteza AN SSSR.

KAGAN, Yu.B.; BASHKIROV, A.N.; KLIGER, G.A.; CHZHOU CHZHAO-DI [Chou Chao-ti];
MAK, N.Ye.

Reaction between octyl alcohols and ammonia under the hydro-
gen pressure on a fused iron catalyst. Neftekhimia 1 no.3:
403-410 My-Je '61. (MIRA 16:11)

1. Institut neftekhimicheskogo sinteza AN SSSR i Institut
tonkoy khimicheskoy tekhnologii imeni Lomonosova.

BASHKIROV, A.N.; KAMZOLKIN, V.V.; SOKOVA, K.M.; ANDREYEVA, T.P.;
KORNEVA, V.V.; ZAKHARKIN, L.I.

Synthesis of cyclododecanol by the liquid-phase oxidation
of cyclododecane. Neftekhimiia 1 no.4:527-534 J1-Ag '61.
(MIRA 16:11)

1. Institut neftekhimicheskogo sinteza AN SSSR i Institut
elementoorganicheskikh soedineniy AN SSSR.

KAGAN, Yu.B.; BASHKIROV, A.N.; KLIGGER, G.A.; CHZHOU CHZHAO-DI
[Chou Chao-ti]; MAK, N.Ye.

Effect of the molecular weight of alcohol on the process
of its amination. Neftekhimiia 1 no.4:555-563 J1-Ag '61.
(MIRA 16:11)

1. Institut neftekhimicheskogo sinteza AN SSSR i Moskovskiy
institut tonkoy khimicheskoy tekhnologii imeni Lomonosova.

33496

S/195/61/002/005/023/027
E040/E185

5.1190

AUTHORS: Kryukov, Yu.B., Bashkirov, A.N., Liberov, L.G.,
Butyugin, V.K., and Stepanova, N.D.

TITLE: On the mechanism of chain growth in the synthesis of
organic compounds from CO and H₂ on iron catalysts

PERIODICAL: Kinetika i kataliz, v.2, no.5, 1961, 780-787

TEXT: A brief survey of the previous investigations of the
synthesis of organic compounds from CO and H₂ mixtures on cobalt
and iron catalysts showed that the mechanism of the chain growth
can be visualised either as 1) condensation of oxygen-containing
complexes, with separation of water, or 2) the growth of the
carbon chain can be assumed as being preceded by the splitting off
of oxygen atoms from the carbon monoxide molecule and a subsequent
chain growth by the mechanism of polymerisation of methyl
radicals. The experimental evidence at present available appears
to be somewhat contradictory and for this reason a study was made
of the role played in the above synthesis by oxygen-free
intermediate complexes of the methyl and hydrocarbon type

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On the mechanism of chain growth...

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E040/E185

radicals. The study was made with the help of radioisotope tracer technique using carbon monoxide labelled with C^{14} carbon (9000 pulse/min per m ℓ). In the tests, a mixture of $C^{14}O + H_2$ (in the 1:1 by volume ratio) was passed over freshly prepared iron catalyst heated to 295 °C, the reaction was allowed to proceed for various periods and the products were then separated. The radioactivity of the separated hydrocarbons was then plotted against the reaction time and the number of carbon atoms in the synthesised hydrocarbons. The results obtained indicated that both the condensation and polymerisation mechanisms are involved in the synthesis of the products. The actual mechanism prevailing at any stage of the reaction was found to depend on the experimental conditions. A general scheme was formulated for the various reactions that can occur when a stream of carbon monoxide/hydrogen mixture is passed over iron catalyst heated to about 300 °C;

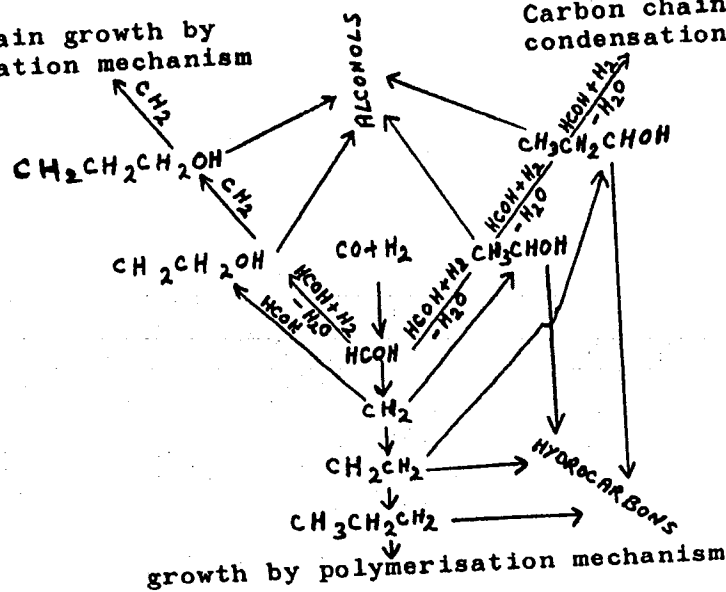
Card 2/4

On the mechanism of chain growth ...

33496
S/195/61/002/005/023/027
EO40/E185

Carbon chain growth by
polymerisation mechanism

Carbon chain growth by
condensation mechanism



Scheme 2

Card 3/4

On the mechanism of chain growth

33496
S/195/61/002/005/023/027
E040/E185

There are 4 figures, 2 schemes and 20 references; 11 Soviet-bloc and 9 non-Soviet-bloc. The four most recent English language references read as follows;

Ref.12: E.J. Gibson, Chem. and Ind., 649, 1957.

Ref.15: G. Blyholder, P.H. Emmett,
J.Phys.Chem., v.63, 962, 1959.

Ref.17: G. Blyholder, P.H. Emmett,
J.Phys.Chem., v.64, 470, 1960.

Ref.18: W.K. Hall, R.J. Cokes, P.H. Emmett,
J.Amer.Chem.Soc., v.82, 1027, 1960.

ASSOCIATION: Institut neftekhimicheskogo sinteza AN SSSR
(Institute of Petrochemical Synthesis, AS USSR)

Card 4/4

Z/011/62/019/001/012/017
E073/E136

AUTHORS: Kamzolkin, V.V., and Bashkirov, A.N.

TITLE: Preparation of higher glycols by oxidation of paraffinic hydrocarbons in the liquid phase

PERIODICAL: Chemie a chemická technologie. Přehled technické a hospodářské literatury, v.19, no.1, 1962, 34, abstract Ch 62-473. (Neftekhimiya, v.1, no.3, 1961, 411-417)

TEXT: The experimental results indicate that during oxidation of paraffin hydrocarbons in the liquid phase in the presence of boric acid, secondary oxidation occurs of monofunctional oxygen compounds to multifunctional. During oxidation of esters by means of acetic acid the proportion of hydroxyl, carbonyl and multifunctional ester groups increases, which leads to the same conclusion. In the presence of acetic anhydride, the described method permits the preparation of glycol esters in addition to keto-alcohols. ✓
1 figure, 4 tables, 7 references.
[Abstractor's note: Complete translation.]
Card 1/1

KAMZOLKIN, V.V.; BASHKIROV, A.N.; SOKOVA, K.M.; MARTYNES, M.; ANDREYEVA, T.P.

Transformations of higher aliphatic alcohols during their
liquid phase oxidation. Neftekhimiia 1 no.5:675-682 S-O '61.
(MIRA 15:2)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Alcohols)(Oxidation)

ROZOVSKIY, A.Ya.; BASHKIROV, A.N.; KAGAN, Yu.B.; POKROVSKAYA, Ye.G.

Water and water vapor oxidation of the iron catalysts for
synthesis from CO and H₂. Kin.i kat. 2 no.6:830-837 N-D '61.
(MIRA 14:12)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Carbon monoxide)
(Hydrogen) (Catalysts, Iron)

ZAKHARKIN, L.I.; KORNEVA, V.V.; KAMZOLKIN, V.V.; SOKOVA, K.M.;
ANDREYEVA, T.P.; BASHKIROV, A.N.

Preparation of ω -dodecalactam from 1,5,9-cyclododecatriene.
Neftekhimia 2 no.1:106-109 Ja-F '62. (MIRA 15:5)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Lactams) (Cyclododecatriene)

KLIGER, G.A.; BASHKIROV, A.N. LYUY GUAN-YUY [LA Kuang-yü]; LESIK, O.A.;
BEZINGER, N.N.; KAGAN, Yu.B.

Method of analyzing products of reaction between aliphatic
alcohols and alkyl amines. Neftekhimia 2 no.1:121-126 Ja-F
'62. (MIRA 15:5)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Alcohols) (Amines)

KAGAN, Yu.B.; BASHIKIROV, A.N.; KLIGER, G.A.; ROZOVSKIY, A.Ya.

Certain problems involved in the microkinetics of amination of
alcohols on fused iron catalysts. Neftekhimiya 2 no.2:253-256
Mr-Apr '62. (MIRA 15:6)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Alcohols) (Amination)

KLIGER, G.A.; BASHKIROV, A.N.; LYUY GUAN-YUY [Lü Kuang-yü]; KAGAN, Yu.B.

Effect of the structure and molecular weight of initial compounds
on the interaction of aliphatic alcohols with primary alkyl
amines. Neftekhimiia 2 no.3:384-390 My-Je '62. (MIRA 15:8)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Alcohols) (Amines)

KAGAN, Yu.B.; BASHKIROV, A.N.; KLIGER, G.A.; LYUY GUAN-YUY [Lü Kuang-yü]

Synthesis of secondary alkyl amines from aliphatic alcohols
and primary amines. Neftekhimiia 2 no.3:391-397 My-Je '62.

(MIRA 15:8)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Amines) (Alcohols)

KAMZOLKIN, V.V.; BASHKIROV, A.N.; KAMZOLKINA, Ye.V.; LODZIK, S.A.

Certain laws governing the liquid-phase oxidation of olefins.
Neftekhimiia 2 no.5:750-755 S-O '62. (MIRA 16:1)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Olefins) (Oxidation)

BASHKIROV, Andrey Nikolayevich

"Obtaining cyclododecanol by liquid-phase oxidation of cyclododecane"

report to be submitted for the 6th World Petroleum Congress,
Frankfurt am Main, W. Germany, 19-26 Jun 63.

ROZOVSKIY, A.Ya.; BIRYUKOVICH, M.M.; IVANOV, A.A.; LIBEROV, L.G.;
BUTYUGIN, V.K.; KAGAN, Yu.B.; KRYUKOV, Yu.B.; BASHKIROV, A.N.

Mechanism of the carbide-forming reaction of fused iron
catalysts for synthesis from CO and H₂. Neftkimiia
3 no.1:97-103 Ja-F '63. (MIRA 16:2)
(Iron catalysts) (Iron carbides)
(Chemistry, Organic—Synthesis)

KRYUKOV, Yu.B.; SMIRNOVA, R.M.; SELEZNEV, V.A.; KAMZOLKIN, V.V.;
BASHKIROV, A.N.

Intermediate stages in the liquid phase oxidation of secondary
alcohols to ketones. Neftekhimiia 3 no.2:238-245 Mr-Apr '63.
(MIRA 16'5)

1. Institut neftekhimicheskogo sinteza AN SSSR imeni A.V.Topchiyeva.
(Alcohols) (Oxidation) (Ketones)

ROZOVSKIY, A.Ya.; IVANOV, A.A.; KAGAN, Yu.B.; BASHKIROV, A.N.

- Kinetics of reactions involving the solid phase. Part 2: Hydrogenation of iron carbides. Kin.i kat. 4 no.1:97-108 Ja-F '63. (MIRA 16:3)

1. Institut neftekhimicheskogo sinteza AN SSSR i Institut tonkoy khimicheskoy tekhnologii imeni M.V.Lomonosova.
(Iron carbides) (Hydrogenation)

ROZOVSKIY, A.Ya.; BIRYUKOVICH, M.M.; IVANOV, A.A.; KAGAN, Yu.B.;
BASHKIROV, A.N.

Kinetics of reactions involving the solid phase. Part 3:
Carbide formation in fused iron catalysts induced by carbon
monoxide. Kin. i kat. 4 no.3:373-381 My-Je '63.

(MIRA 16:7)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Carbides) (Iron catalysts)
(Chemical reaction, Rate of)

S/020/63/148/006/014/023
B117/B186

AUTHORS: Bashkirov, A. N., Corresponding Member AS USSR,
Shaykhutdinov, Ye. M., Gilyarovskaya, L. A.

TITLE: Oxidation of monomethylsubstituted paraffins in liquid phase
in the presence of boric acid

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 148, no. 6, 1963, 1309 - 1311

TEXT: The effect of the tertiary carbon atom on the conversion of mono-substituted paraffins during oxidation and on the composition of the alcohols formed is studied. For this purpose, 2-methyldodecane and 8-methylpentadecane were synthesized according to Grignard's method. These hydrocarbons were oxidized in an apparatus described previously (A. N. Bashkirov, Khim. nauka i prom., 1, 273 (1956)) under normal pressure at 165 - 170°C for 3 - 4 hrs, using a mixture of nitrogen and oxygen with 3.0 - 3.5% O₂ (consumption 800 l/kg·hr). The main conversion products were compounds containing hydroxyl with a yield of ~75 mole%. The alcohols formed were identified as a mixture of tertiary (~25 - 30 mole%) and secondary alcohols having the same carbon skeleton and the same number of C-atoms in the molecule as the original hydrocarbon. The secondary
Card 1/2

Oxidation of monomethylsubstituted...

S/020/63/148/006/014/023
B117/B186

alcohols proved to be a mixture of a variety of isomers. Hence it was assumed that, under the oxidation conditions described, the tertiary C-atoms are more reactive with respect to oxygen than the secondary C-atoms of the highest monosubstituted paraffin molecules. There are 3 tables.

ASSOCIATION: Institut neftekhimicheskogo sinteza Akademii nauk SSSR (Institute of Petrochemical Synthesis of the Academy of Sciences USSR); Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M. V. Lomonosova (Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov)

SUBMITTED: July 26, 1962

Card 2/2

NEVOLIN, Fedor Vasil'yevich; TYUTYUNNIKOV, B.N., doktor tekhn. nauk, prof., retsenzent; BASHKIROV, A.N., spets. red.; MOROZOVA, I.I., red.

[Chemistry and technology of synthetic detergents] Khimiia i tekhnologiya sinteticheskikh moiushchikh sredstv. Moskva, Izd-vo "Pishchevaia promyshlennost'," 1964. 362 p.
(MIRA 17:7)

1. Chlen-korrespondent AN SSSR (for Bashkirov).

ACCESSION NR: AP4024408

S/0204/64/004/001/0106/0110

AUTHOR: Kagan, Yu. B.; Bashkirov, A. N.; Kliger, G. A.; Lu, Kuang-yu

TITLE: Synthesis of secondary alkylamines from carbon monoxide, hydrogen and methylamine.

SOURCE: Neftekhimiya, v. 4, no. 1, 1964, 106-110

TOPIC TAGS: secondary alkylamine, synthesis, amination, process condition, reaction mechanism, methylalkylamine

ABSTRACT: Continuing earlier work (Yu. B. Kagan, A. N. Baskirov, G. A. Kliger, Yu. I. Yermakov, Izv. AN SSSR, Otd. khim. n. (1959), 1345), the interaction of CO, H₂ and methylamine to form secondary alkylamines was studied. Using a fused iron catalyst, the optimum synthesis conditions are 100-140 atmospheres pressure, 1250 hours⁻¹, volume flow of the initial gas mixture, a temperature of 168-175 C, and an H₂:CO:CH₃NH₂ ratio of 4:1:1.25. The yield of secondary amines was 77-78.5 mol.%. The product also contained small amounts of alcohols and carbonyl compounds, indicating the synthesis probably proceeded in two stages; (1) the formation of the oxygen-containing compounds from CO and H₂, (2) followed by

Card 1/2

ACCESSION NR: AP4024408

their amination with methylamine. The aminated products are 5-20 carbon atom methylalkylamines of normal structure. Synthesis of secondary amines by this method was realized for the first time. Orig. art. has: 6 tables.

ASSOCIATION: Institut neftekhimicheskogo sinteza AN SSSR im. A. V. Topchiyeva
(Institute of Petrochemical Synthesis, AN SSSR)

SUBMITTED: 03May63

DATE ACQ: 17Apr64

ENCL: 00

SUB CODE: GC

NO REF SOV: 007

OTHER: 008

Card 2/2

LOKTEV, Sergey Minovich; BASHKIROV, A.N., otv. red.

[Higher aliphatic alcohols] Vysshie zhirnye spirty. Moskva, Nauka, 1964. 165 p. (MIRA 17:10)

1. Chlen-korrespondent AN SSSR (for Bashkirov).

KAMZOLKIN, V.V.; BASHKIROV, A.N.; SOKOVA, K.M.; ANDREYEVA, T.P.

By-products of the liquid-phase oxidation of cyclododecane with
molecular oxygen in the presence of boric acid, *Neftekhimiya*
4 no.1:96-99 Ja-F'64 (MIRA 17:6)

1. Institut neftekhimicheskogo sinteza AN SSSR imeni A.V.
Topchiyeva.

KAGAN, Yu.B.; BASHKIROV, A.N.; GLIGER, G.A.; LYUY GUAN-YUY

Synthesis of secondary alkylamines from carbon monoxide, hydrogen,
and methylamine. Neftekhimiia 4 no.1:106-110 Ja-F'64

(MIRA 17:6)

1. Institut neftekhimicheskogo sinteza AN SSSR imeni A.V.
Topohiyeva.

ROZOVSKIY, A. Ya.; BIRYUKOVICH, M.M.; IVANOV, A.A.; KAGAN, Yu.B.; BASHKIROV,
A.N.

Kinetics and mechanism of the carbidizing treatment of iron
catalysts for synthesis from CO and H₂. Neftekhimiia 4 no.2:
269-274. Mr-Apr'64 (MIRA 17:8)

1. Institut neftekhimicheskogo sinteza AN SSSR imeni Topchiyeva.

BASHKIROV, A.N.; KAMZOLKIN, V.V.; POTARIN, M.M.

Obtaining higher ketones by the dehydrogenation of secondary
alcohols over copper-chromium and nichel-chromium catalysts.
Neftekhimiya 4 no.2:298-300 Mr-Apr'64 (MIRA 17:8)

1. Institut neftekhimicheskogo sinteza AN SSSR imeni A.V. Topchi-
yeva.

NOVAK, F.I.; KAMZOLKIN, V.V.; BASHKIROV, A.N.

Catalytic activity of the natural silicates of minerals in the
synthesis of hydrocarbons from carbon monoxide and hydrogen.

Neftekhimia 4 no.3:447-451 My-Je '64.

(MIRA 18:2)

1. Institut neftekhimicheskogo sinteza AN SSSR im. A.V.Topchiyeva.

BASHKIROV, A.N.; ALENT'YEVA, Ye.S.

Liquid-phase oxidation of alkyl benzenes in the presence of esterifying agents. Neftekhimia 4 no.4:593-598 J1-Ag '64. (MIRA 17:10)

1. Moskovskiy institut tonkoy khimicheskoy tekhnologii im. M.V. Lomonosova i Institut neftekhimicheskogo sinteza im. A.V. Topchiyeva AN SSSR.

6-35416-63 $\text{E}(\text{T}(u))/\text{E}(\text{NP}(j))/\text{E}(\text{NP}(n))$ $\text{Pc-L}/\text{Pr-L}$ Ru-L

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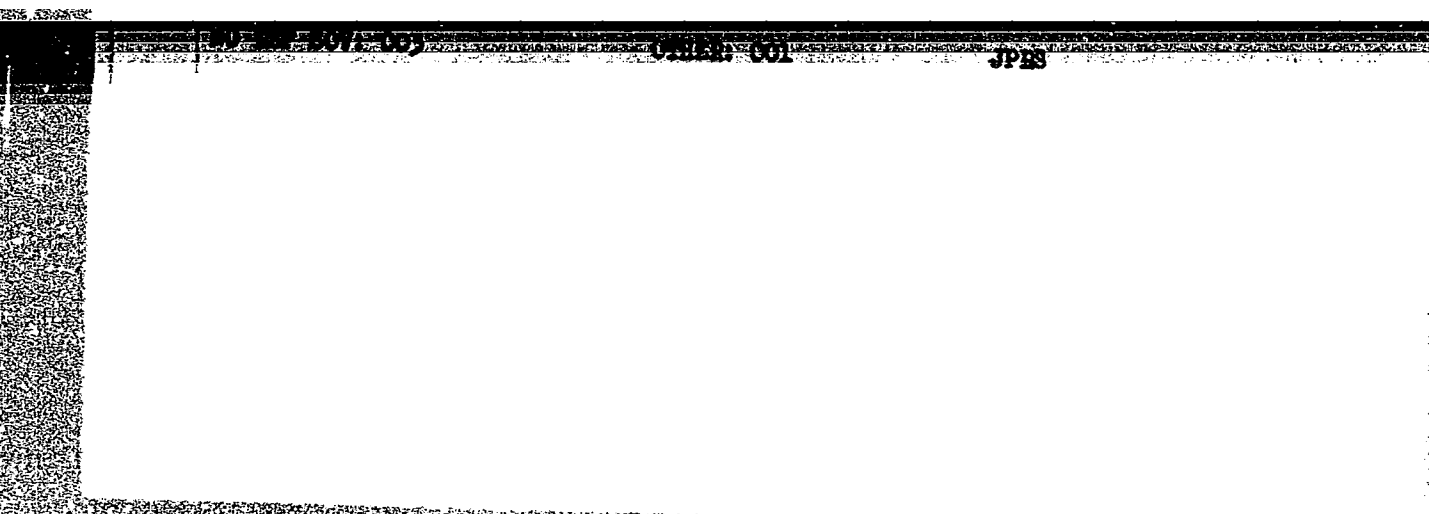
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BASHKIROV, A.N.; GILYAROVSKIY, L.A.; ALENT'YEVA, Ye.S.; KOZLENKOVA, R.V.;
KUROCHKINA, A.K.

Effect of aromatic hydrocarbons on the oxidation of paraffins in the
liquid phase in the presence of boric acid. Neftekhimiya 4 no.5:777-
779 S-O '64. (MIRA 18:1)

1. Moskovskiy institut tonkoy khimicheskoy tekhnologii imeni M.V.
Lomonosova i Institut neftekhimicheskogo sinteza imeni A.V.Tepchiyeva
AN SSSR.

L 15673-65

EWI(m)/EPF(c)/EXP(3)/T/EXP(1)/EXP(1)

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ASSOCIATION: Institut neftekhimicheskogo sinteza im. A. V. Topchiveva, AN SSSR

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